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EXAMINATION OF TREATMENT METHODS FOR CYANIDE WASTES

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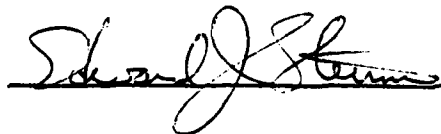APR 2 1 1980

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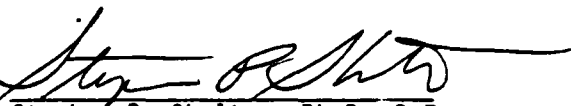Report No. NADC-78198-60   15 May 1979

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SUMMARY

Introduction

An investigation into the current state of the knowledge methods for treatment of cyanide electroplating wastes was conducted as related to Naval Air Rework Facilities. This effort was limited to a desk audit of available technical literature and commercial data and no laboratory evaluations were performed. Over 250 journal articles from nine countries were reviewed and ninety-eight articles considered germane to the Naval problems were incorporated into the review to evaluate the effectiveness of cyanide waste treatment as related to concentration and destruction techniques. Processes that appeared to have potential on initial review that were subsequently found to be inadequate are also discussed. Both integrated treatment and in process treatment were considered and were applicable combination treatments. For treatment methods selected, a detailed study of chemical and mechanical technology, process flow, economics, effectiveness, operational requirements, process hazards and overall process potential was accomplished. For those treatment processes that were deemed unacceptable for Naval application, the reasons for rejection are discussed.

Discussion of Results

Of the processes evaluated there are two major categories of treatment techniques that were determined to be germane to the interest of the Navy :
concentration techniques, which included ion exchange and evaporation; and destruction techniques, which included alkaline chlorination, electrolytic chlorination, ozonation, electrolytic decomposition, and waste plus waste.
Destruction processes considered, but subsequently rejected due to infeasibility from either process or economics, included acidification, activated carbon absorption, biodestruction, dilution and ponding, electrodialysis, high pressure and temperature destruction, hydrogen peroxide, ion flotation, polymerization, radiation, selective concentration method for gold,silver

and copper, solvent destruction, and starch conversion syrup.

Conclusions

Of the processes recommended for potential application at Naval Air Rework Facilities, the most common ongoing and anticipated future process for cyanide destruction is alkaline chlorination. This process, however, should not be used exclusively but should be evaluated as a function of its capabilities. The two processes that were identified that may eventually overtake alkaline chlorination as preferred processes would perhaps be evaporation and electrolytic chlorination. Evaporation has the distinct advantage that the discharge is totally eliminated and thus the problem of meeting stringent effluent criteria for discharge of cyanides and cyanide waste would be thereby eliminated. A further advantage of this process is that the cyanides in the waste stream are recovered and can be reused as well as the water that is recovered in the evaporation process.

The primary disadvantage of evaporation techniques are associated with the energy requirements to evaporate the cyanide wastewater. This will preclude cavalier use of the evaporation as a wastewater treatment technique; however, it will not preclude use of evaporation as a technique for cases wherein other techniques, either concentration or distruction, are unable to meet requisite effluent requirements. Furthermore, it is often times possible in a large industrial complex to utilize waste heat for this evaporation process since it is not required to be a continuous operation. Thus energy that is available during nonpeak periods can be utilized to power the evaporation unit. Furthermore, it may be possible to concentrate cyanide waste extensively using them as scrubber water makeup. This can be practical as long as pH conditions are maintained so that hydrogen cynanide gas is not formed.

Regarding the potential use of electrolytic chlorination as a treatment method for cyanide wastes, the distinct advantage realized by this method is the substitution of sodium chloride for chlorine gas as the reactive agent. This greatly simplifies

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materials handling and safety considerations associated with chlorine gas that are always a problem in industrial operations.

Recommendations

It is recommended that selection of treatment methods for cyanide concentration or destruction should be predicated upon the least costly system that would be functional for the purposes intended. Of the seven processes identified as potentially useful to Naval Air Rework Facilities, it is envisioned that alkaline chlorination will remain the most commonly utilized cyanide treatment process. (See Table However, with the recent advancements in chlorine cell construction techniques, the electrolytic chlorination process, which works in essentially the same manner as the alkaline chlorination process, may replace the alkaline chlorination process as the preferred method within the next few years. It is further noted, that with the continued increases in effluent requisite water quality requirements that the ion exchange and evaporation processes, discussed under concentration techniques, are likely to be the processes of choice when attempts to minimize or eliminate effluent discharges from cyanide processes become a major concern to the Navy. These processes are however high energy users and thus should be throughly evaluated before use.

Although this report reviewed a dearth of technical literature, the reliability of the processes identified is uncertain. It is recommended that pilot level field testing be performed to assure that the more unique processes will be functionally operative and thus meet the needs of the Naval Air Rework Facilities.

DISCUSSION

This investigation was designed to provide a state of the knowledge report for the treatment of cyanide wastes generated by Naval electroplating facilities. The effort was limited to a desk audit of available technical literature and commerical data. It was not intended that this investigation should consider any of these processes in the laboratory mode. The cyanide waste treatment methods were screened for potential application to Naval industrial processing and those systems that were identified to have promise as potential waste treatment systems for Naval Air Rework Facilities and other Navy industrial operations were investigated in detail. Over 250 literature citations were reviewed, of which ninety-eight were considered germane to the needs of the Navy. Each of these ninety-eight articles was reviewed in detail, considering both integrated treatment systems in process and process effluent treatments. For each method of treatment selected for detail study, advantages, disadvantages, costs, hazards, and process effectiveness were considered. For each treatment method chosen for further study,that was subsequently determined to be unacceptable for Navy use, a detailed evaluation is also provided.

There are two primary directions to proceed in the abatement of pollution due to cyanides from Navy electroplating facilities; concentration of the cyanide waste with reclamation or disposal of the concentrated wastes, or destruction of the cyanides to some less objectionable form. From the literature review, two acceptable concentration techniques and five acceptable destruction techniques were identified. In addition, thirteen process techniques for cyanide destruction were reviewed in detail and subsequently rejected due to either cost, effectiveness, or hazardous by-products generated by these processes.

In discussion of the concentration techniques, the two techniques considered acceptable for the Navy needs, include ion exchange and evaporation. The ion exchange technique is primarily suitable for dilute rinse wastes. These wastes are pumped through a chamber containing an ion exchange resin. The resin is a

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polymeric substance with a high molecular weight that has the ability to selectively exchange ions between itself and liquid with which it is in contact. This process is effective in the concentration of cyanide wastes from dilute rinses up to 2000 milligrams per liter as free cyanide. This process is also effective on mixtures of free, complexed and precuror cyanide compounds. The pH of this process is operated in the 4-7 range which has the potential to cause problems with the generation of hydrogen cyanide gas. The pH is maintained above 8 prior to the treatment process. Process efficiency decreases as the exchange capacity of the resin is reduced prior to regeneration. It is further noted that disposal of ferrous hydroxide in cyanide sludges, generated during the regeneration process of the resin, may be difficult to dispose of unless a reprocessor can be located. Low level operator skill is required, specifically that level which is sufficient to maintain pH control. The second concentration process, evaporation, shows significant merit as a potential process for application at Naval electroplating facilities. This technique is applied to plating lines using countercurrent rinsing. A single effect evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the plating bath and distilled water from the evaporation system is returned to the final rinse tank. It is noted that the great advantage of this recovery system is its zero discharge attribute; thus the only plating chemicals added to the bath are those that replace chemicals actually deposited on the parts or lost by spillage and dragout. It appears that the capital investment and labor on this type of system would be relatively small by comparison to most treatment alternatives; however, the process is designed for dilute rinses only and treatment for concentrated bath dumps would have to be provided. Furthermore, the operating cost (energy) is high and thus should be carefully considered. As with the ion exchange system, the level of operator training is rather low requiring only skill in the control of pH. The only process hazard associated with this operation is the generation of hydrogen cyanide gas, which is a problem with all cyanide treatment processes. For this reason, the control of pH is critical. A primary

disadvantage of this system, as with all recovery systems, is that the cyanide waste must be segregated totally from all other waste streams since the materials recovered must be of sufficient quality to allow reintroduction to the system.

As previously mentioned, five destruction techniques were considered to be of interest to the Navy for treatment of cyanide contaminated electroplating wastewaters. These techniques included alkaline chlorination, electrolytic chlorination, ozonation, electrolytic decomposition, and waste plus waste. Of these five processes, the most common treatment process in use and probably the process of preference for cyanide treatment, in the electroplating industry, is alkaline chlorination. This process oxidizes cyanide to cyanate followed by complete decomposition yielding carbon dioxide and nitrogen or ammonium salts, depending upon the final treatment methods. Normally, the oxidizing agent used is chlorine gas, however, hypochlorites have been used successfully. In order for this process to work safely, the reaction must be performed in the alkaline range at a pH greater than 10. To accomplish this, a substantial amount of solid or liquid caustic is necessary to maintain tne proper pH of the solution and to prevent the formation of toxic cyanogen chloride and hydrogen cyanide gas. The overall process is highly effective and relatively inexpensive. However, the hazardous chlorine by-products and hydrogen cyanide gas potential is always of concern. Effluent concentrations generated are below maximum allowable limitations on toxic materials; however, sludge formation from time to time can be a problem. Another shortcoming of alkaline chlorination treatment is that if a substantial amount of cyanide is complexed with iron or nickel, the reaction is relatively slow, thus, the cost of treatment per unit is increased substantially. In these instances, one of the alternative cyanide treatment methods, to be discussed subsequently, should be considered in lieu of alkaline chlorination.

A modification of the alkaline chlorination approach to cyanide waste treatment is accomplished in a process called electrolytic chlorination. In this process, the cyanides are reacted with chlorine under alkaline conditions and the reactions proceed in a manner similar to those of alkaline chlorination; however, the chlorine

is not added to the system, it is produced within the system using an electrolytic cell and a one to three per cent solution of magnesium chloride (or sodium chloride) salt. Since the production of chlorine is a function of the amount of energy supplied to the electrolytic cell and the caustic is a by-product of the salt reaction in the production of the chlorine, the flexibility derived from this system is extremely advantageous. It has been shown, that this type of approach is a viable treatment alternative for cyanide concentrations as low as 3 mg/l (milligrams per liter) and as high as 70,000 mg/l at 20 $^{\circ}$C. As with all cyanide treatment processes, this process is not without some hazards. Since the chlorine is generated by electrolytic process, a small amount of hydrogen gas is formed during the conversion. This gas can be removed by venting the gases into the chlorine tank. The entire system should have a pH, cyanide, and chlorine monitoring network to prevent the incomplete destruction of the cyanides that are present. If the system is designed to treat cyanides to a low level, then some caustic storage may be required since caustic generation may exceed requirements. Since the caustic generated in the system must be handled, corrosive resistant materials and caustic handling procedures must be followed.

Oxidation of cyanides to cyanates by ozonation is a potent treatment method for simple cyanides and disassociated zinc, cadmium, silver, copper and nickel complexes; however, like alkaline chlorination, the more stable cyanides such as iron are difficult to oxidize. A substantial improvement in the ability of ozone to oxidize the more difficult complexes is obtained if the ozone is applied in combination with ultraviolet radiation at elevated temperatures. The ozone processes have a substantial benefit in that they are extremely flexible in obtaining acceptable treatment levels for widely varying concentrations; however, the cost of the processes,in terms of operating and capital investment costs per pound of cyanide destroyed,are approximately four to five times that of alkaline chlorination. This cost, in most circumstances, would preclude the use of ozonation as a viable process for cyanide treatment. As with all cyanide processes, production of hydrogen

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cyanide gas is always a potential hazard.

Electrolytic decomposition is a process that has potential application for cyanide destruction, especially for waste streams that are of mixed character. This process provides a treatment vessel, such as a packed bed electrochemical cell, that collects the cationic metals upon the particles in the packed bed and the cyanide is oxidized in the anionic bed. The resulting process effluent contains low concentrations of both metals and cyanide. Nickel is sometimes used as catalyst to enhance the reaction. This process generally presents less of a hazard of hydrogen cyanide gas production since the pH is not modified during the process. This treatment method is generally economical only when high concentrations of cyanide (in excess of 1,000 mg/1 and up to 100,000 mg/1) exist. The cost of this treatment process is somewhat higher than the alkaline chlorination type processes and the ozone process; however, since the potential for the recovery of metals is available with this treatment method, unlike previous methods discussed, a substantial savings could be realized if precious metals were involved.

The waste plus waste process uses a method that is designed to treat one waste by utilization of a second waste and also realize recovery of most of the metal contained in both streams. One of the waste solutions must be alkaline, containing cyanide and dissolved metals, while the other solution must be acidic and may contain other dissolved metals. The process centers around the addition of the acidic waste to the alkaline liquid waste, under homogeneous mixing conditions, to avoid the formation of hydrogen cyanide gas. Batch processing is the usual mode of operation and the final product contains metal cyanides and dilute solutions of metal ions, which may be precipitated out and recovered. pH is critical in this process and maintenance of the pH between 5.5 and 7.5 is required. Knowledge of specific metal types of concentrations in all wastewaters, is required for correct combining of the wastes of concern. The temperature of reaction is also an important consideration in this process. As can be imagined, the operational

requirements of this type of system are such that, a substantial amount of training would be required for the operators to facilitate adequate control over the recovery process and to avoid the hazards inherent in the addition of acidic wastes to cyanide bearing wastes. The process has been shown to be effective in the treatment of both low and high concentrations of cyanide wastewaters; however, the cost of highly trained operators and the cost of disposal of unusable toxic metallic cyanide sludges may preclude use of this method.

Thirteen other destruction techniques were reviewed and discarded as unacceptable for Naval needs. These processes and the reason for their rejection is contained in the Appendix III of this report.

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APPENDIX

I. <u>Concentration Techniques</u>

Concentration techniques do not eliminate cyanides, but remove them from the rinse tanks where they accumulate due to drag-out and put them in a form whereby they may be reused. An added benefit of these methods is that,in addition to the cyanides, the metals being plated are also returned to the baths. This metal return reduces the periodic addition of chemicals, thus lowering materials costs and eliminating the need to dispose of large quantities of dilute wastewater. Concentration techniques are not applicable for the disposal of concentrated bath solutions. Another major disadvantage is that a duplicate system must be built for each group of bath and subsequent rinse tanks.
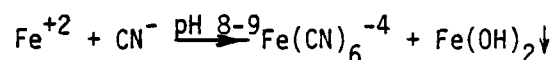
1. Ion Exchange

   a. Process Description

In this process the dilute rinse wastes are pumped through a chamber containing an ion exchange resin. The resin is a polymeric substance of high molecular weight that has the ability to selectively exchange ions between itself and the liquid it contacts. Cationic and anioic resins exist, and have been incorporated into experimental systems. The cationic resins have sulfanic and carboxylic ion-active groups while the anionic groups are primary, secondary and tertiary amines. During the process, the ion exchange sites become saturated and efficiency decreases. When a critical level is reached the resin is regenerated in order to release the trapped ions and make available the exchange sites. Anionic resins are restored with alkaline compounds while cationic resins use acids.

There are several varieties of ion exchange methods. In this instance the most promising involved using the ferrous ion as a
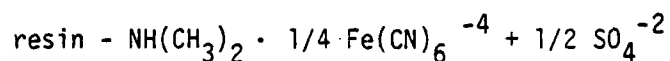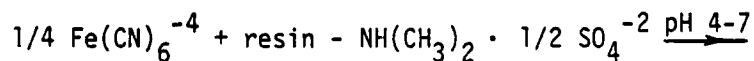
complexing agent. The ferrous ion incorporates all of the cyanide into anionic ferrocyanide ($Fe(CN)_6^{-4}$). The advantage of this is that iron complexes are stable at all pH's of water and they will not readily decompose.

A macroreticular weak-base anion exchange resin, known as AMBERLITE XE-275 (a registered trademark of Rohm and Haas Company) selectively removes all of the ferrocyanide present. Any excess iron will precipitate out at the pH's of complex formation and may be removed.

The initial reaction is: (See Figure 1.)

$$Fe^{+2} + CN^- \xrightarrow{pH\ 8-9} Fe(CN)_6^{-4} + Fe(OH)_2\downarrow$$

The ferrocyanide produced is selectively removed by the ion exchange resin Amberlite XE-275, operating in the acid salt form. The next step is:

$$1/4\ Fe(CN)_6^{-4} + resin - NH(CH_3)_2 \cdot 1/2\ SO_4^{-2} \xrightarrow{pH\ 4-7}$$

$$resin - NH(CH_3)_2 \cdot 1/4\ Fe(CN)_6^{-4} + 1/2\ SO_4^{-2}$$

When the resin is completely loaded, it may be regenerated with dilute sodium hydroxide (1-10% solution) producing a concentrated cyanide sludge:

$$resin - NH(CH_3)_2 \cdot 1/4\ FE(CN)_6^{-4} \xrightarrow{NaOH}$$

$$resin - NH(CH_3)_2 + Na_4Fe(CN)_6 + H_2O$$

21
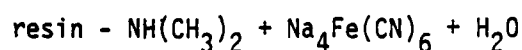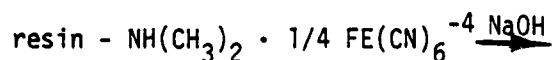
Then the resin must be converted back to the protonated amine salt
form for the next cycle. Conversion is done adding dilute sulfuric
acid:

$$\text{resin} - NH(CH_3)_2 + 1/2\ H_2\ SO_4 \longrightarrow$$

$$\text{resin} - NH(CH_3)_2 \cdot 1/2\ SO_4^{-2}$$

Regeneration

Fe SO₄

Sand
Filter

pH 4-7

NaOH

PH
8-11

Cyanide
Waste
Stream

Clari-
fier

Weak
Base
Resin
(SO₄)⁼

Weak
Base
Resin

Fe(OH)₂ Sludge

Cyanide
Free
Waste
(To Sewer)

Na₄ Fe(CN)₆
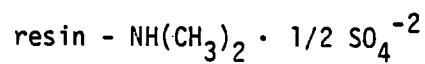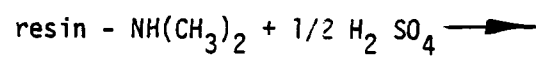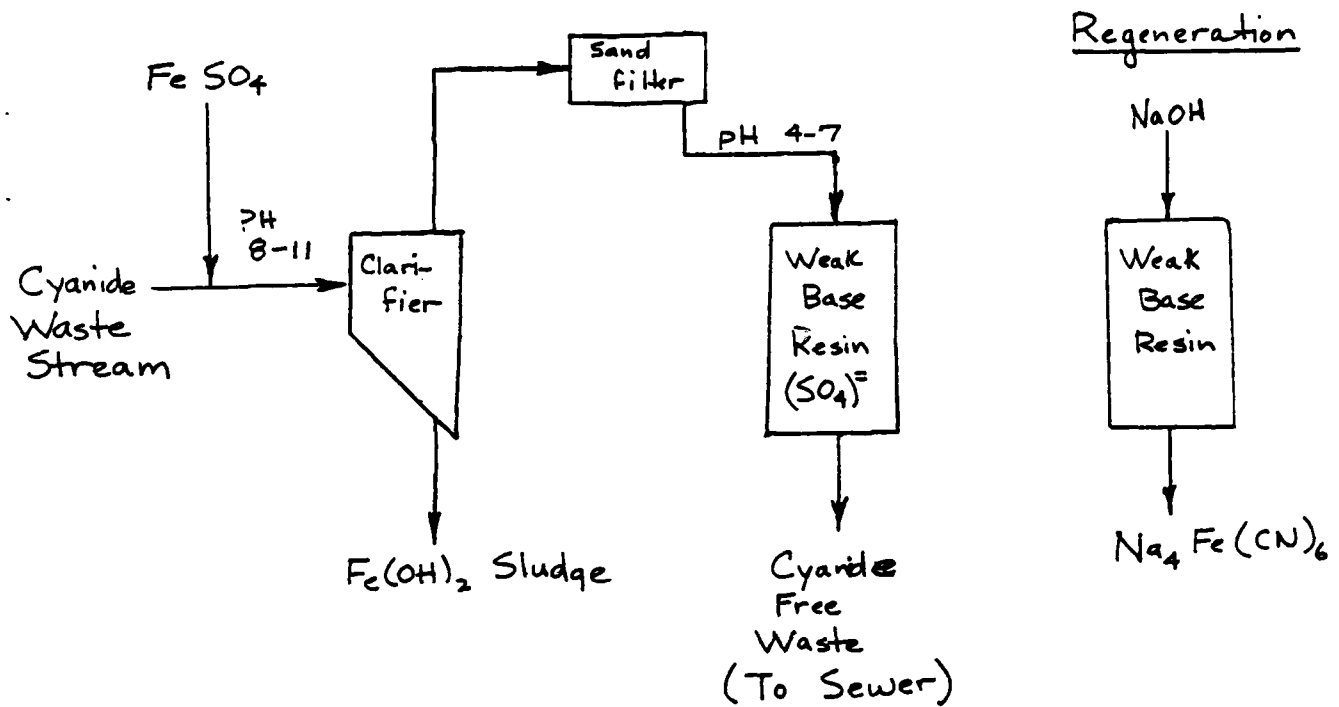
Selective Removal of Cyanide
By Ion Exchange.
(Figure # 1)

b. Treatment Parameters

Concentration of cyanides that have been tested for this process, are up to 2,000 ppm as free or mixtures of free, and complexed precurors. The pH into the clarifier should be between 8 and 11 and the solution pH must be adjusted between the 4-7 range prior to the absorption step. The resin pH can be adjusted without chemical addition by leaving a quantity of resin unconverted ($\sim$ 10%). The process is operated at room temperature and flows are limited to the maximum volume allowable through the resin beds. Maximum system efficiency can be obtained at lower cyanide concentrations (< 50 ppm). Sources of sodium hydroxide, sulfuric acid and ferrous sulfate must be provided. Excess iron precipitate and cyanide sludge must be collected.

c. Economic Survey

Disposal of ferrous hydroxide and cyanide sludge will increase costs,unless provision is made to sell the material. Supervision of system is needed and may require more than one individual to maintain operation. The exact cost of materials will depend on the particular system and design needs.

d. Operational Requirements

There is no special training required except, knowledge of pH control and resin capabilities. Maximum flow levels are restricted to the amount of time necessary for ferrocyanide removal. Amberlite XE-275 was indicated to be an excellent resin,with very easy regeneration abilities with dilute sodium hydroxide. Possible fouling from solids may require monitoring and possible system filtration (a sand filter was used in flow diagram).

e. Process Hazards

The complete complexing of cyanides with iron is necessary
to prevent excess cyanide concentration in effluent. If absorption pH
is not kept above 4, the formation of blue cyanide precipitate
may occur which will pass completely through the system. Control
of pH is important to insure maximum efficiency, and to prevent
formation of hydrogen cyanide gas. Suspended solids may clog
resin unless filtering is provided. The resulting effluent leveis
of cyanide, for dilute concentrations and low flow conditions, were
below .1 mg/l total CN.

f. Process Effectiveness

This process seems to be most suitable for small flow and
concentration systems,like those that would be found in rinse tank
purification. The major costs would be regenerated chemicals and
cost effectiveness to other systems will have to be carefully com-
pared. Ion exchange should prove less expensive than other currently
used methods, especially alkaline-chlorination. The life of resins
and regeneration capacities need to be studied in more depth,before
an accurate cost comparison and treatment effect can be made.

(References cited: 1, 4, 19, 33, 37, 64, 69, 80, 89, 92 93).

2. Evaporation

 a. Process Description

 This technique is applied to plating lines using counter-
current rinsing. A single effect evaporator concentrates flow from
the rinse water holding tank (see Figure # 2). The concentrated
rinse solution is returned to the plating bath, distilled water is
returned to the final rinse tank. In this recovery system no
external rinse water is added except to make up for evaporation.
The only plating chemicals added to the bath are those for replacing
what is actually depositied on the parts, any spillage or accidental
losses. This system recovers nearly 100% of the plating chemicals
normally lost in dragout. If a counter-current rinse system is
not used, an open loop evaporative system has been developed which
does not recover all of the wastes. This system was not considered
since it required secondary treatment for effluent rinse cyanide
concentrations.

 b. Treatment Parameters

 The treatment process is basically automatic with nominal
maintenance required. Concentration and flow is regulated by the
system capacity. Storage tanks for wastes to be treated eliminate
the possibility of shock loading. The system pH and temperature
are monitored to prevent possible hydrogen cyanide production.
Separate systems for each group of bath and rinse tanks are required
since bath mixtures cannot be combined.

 c. Economic Survey

 Capital investment and labor can be amortized in two to three
years considering the savings of plating chemicals. There is no
effluent or sludge produced, so disposal costs are also removed.
This process is for dilute rinse treatment only, and concentrated
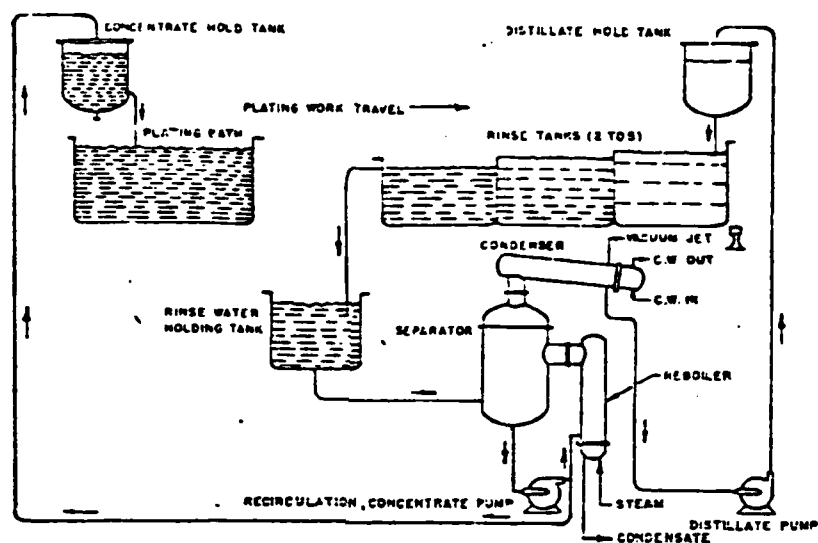
Cyanide recovery system with single effect evaporator.

(Figure #2)

bath treatment will have to be provided. If dual treatment of bath and
rinse tanks is expected, this system could be a possible choice, if the
savings in chemicals and water would be significant enough to offset
the energy requirements to operate the evaporation system on a nonenergy
peak usage intermit basis. If the energy requirements, however, are such
that the trade off between the savings in chemicals, and the cost of energy
are not economical, this system must be discarded.

d. Operations Requirements

No special training or requirements are necessary for this system. If it
is controlled, the general maintenance and inspection should be minimal.
Production of toxic materials can be prevented by pH and concentration warning
devices.

e. Process Hazards

There are no unusual hazards for this system except HCN production. Steam
is necessary for one portion of the treatment process and safety precautions
should be observed. Since this process concentrates all of the chemicals in
the rinse tank, there is a possibility of bath contamination, and bath
replacement may be more frequent to keep quality levels high.

f. Process Effectiveness

This system is highly efficient in treating dilute cyanide concentrations.
Heavy metal recovery approaches 100% and no effluent is produced. Cyanides are
preserved and reused in the plating process. Economics of this
system are favorable if metal recovery is important. The requirement of a
separate treatment for each operation may limit the applicability of this
system to smaller operations. Also, a bath treatment process is necessary for
complete removal of the entire waste cyanide production.
(References cited: 5, 28, 37.)

II. Destruction Techniques

1. Alkaline Chlorination

a. Process Description

The most widely used method of cyanide treatment is alkaline-chlorination. This process oxidizes cyanide to cyanate followed by complete decomposition yielding carbon dioxide and nitrogen, or ammonium salts depending on final treatment methods. The major oxidizing agents that have been successfully used are chlorine gas and hypochlorites. When chlorine gas is used as the oxidizing agent, the initial chemical reaction is:

$$XCN + 2\ NaOH + Cl_2 \longrightarrow XCNO + 2\ NaCl + H_2O$$
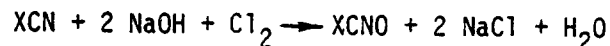
This reaction takes place in an alkaline cyanide solution of pH preferably 10 or higher. The addition of solid or liquid caustic is necessary to maintain proper pH of solution and prevent the formation of very toxic cyanogen chloride. Oxidation of cyanides to cyanates proceeds rapidly; however, there is considerable metal precipitation and sludge formation. The complete destruction of cyanides can be accomplished by lowering the pH of the solution to between (7.5 - 9.0) and added excess chlorine. This step is:

$$2XCNO + 4NaOH + 3Cl_2 \longrightarrow 2XCl + 4NaCl + 2CO_2 + N_2 + 2H_2O$$
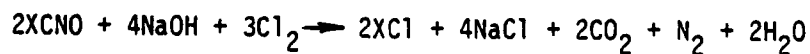
(X represents a cation.)

29

This liberates carbon dioxide and nitrogen gas as end products. Possible acid hydrolysis has been described using sulfuric acid to produce ammonium salts:

$$2NaCNO + H_2SO_4 + 4H_2O \longrightarrow (NH_4)_2SO_4 + 2NaHCO_3$$
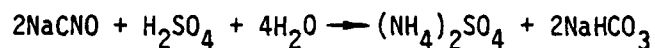
This is accomplished at a low pH (1-3) and elevated temperatures. The entire process, from cyanide to end products, is relatively short. Treatment time is solution dependant, with stable metal-cyanide complexes requiring longer detention time.

Figure # 3 shows an automated batch process whereby the waste is circulated until the required pH is reached.

Shown in Figure # 4 is a continuous or flow through system with automatic control. The waste is balanced and smoothed, then delivered to receiving chamber.

Hypochlorites have also been successfully used as oxidizing agents. The basic reactions are similar, but equivalent amounts of chlorine, in the hypochlorite radical, are necessary. A typical reaction:

$$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$$
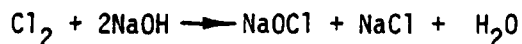
It requires a greater amount of hypochlorite to destroy one pound of cyanide due to the smaller percentage of chlorine, by weight, in the hypochlorite compound.

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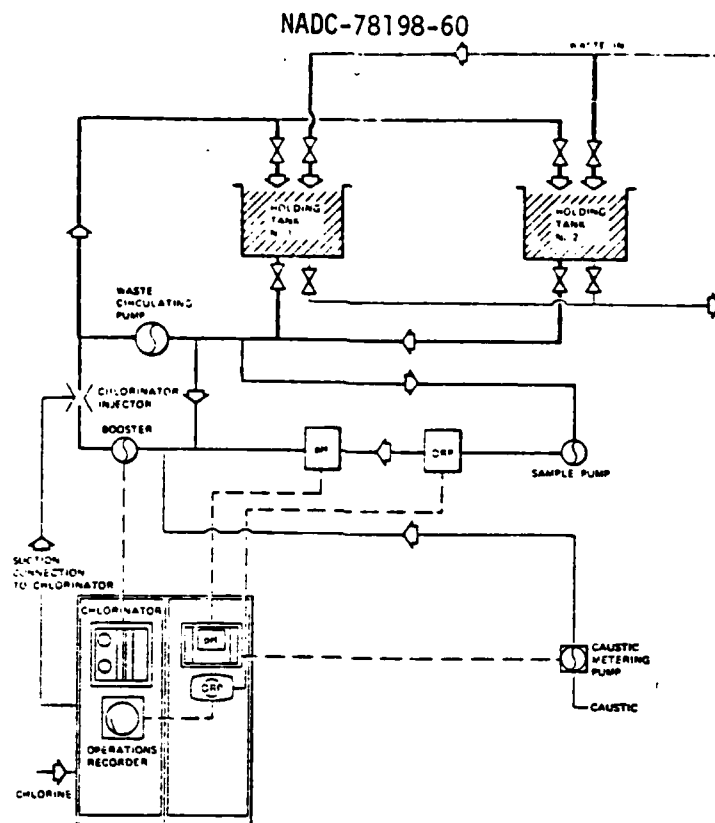
Automated Batch Processing
(Figure # 3)
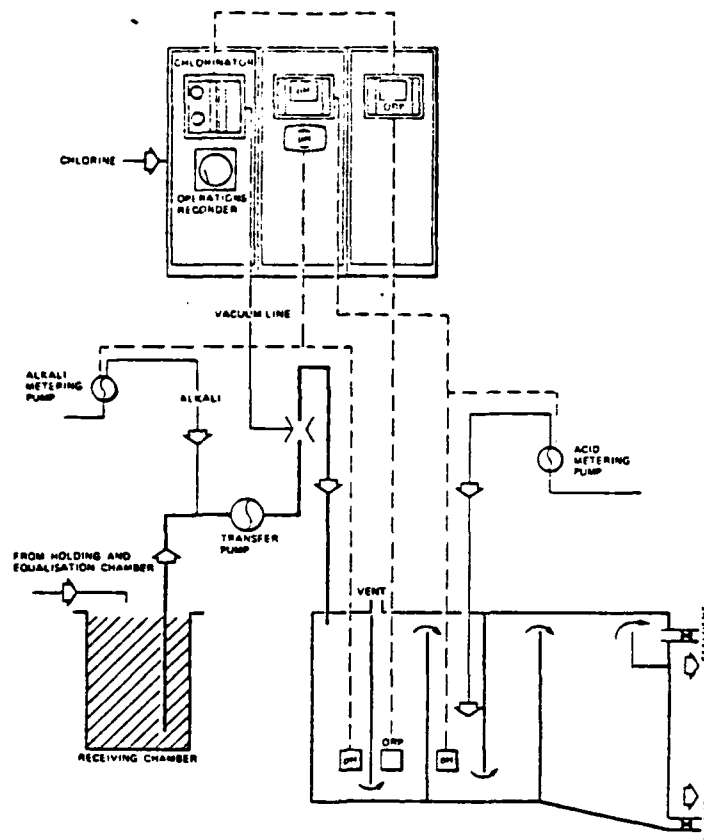
Flow through system
with automatic control
(Figure # 4)

b. Treatment Parameters

The general treatment procedure is similar for both chlorine gas and hypochlorites. Both processes are operated at room temperature and controlled pH with constant mixing and agitation. The reagent requirements apply whether or not metallic ions are present, and are as follows:

Oxidation of cyanide to cyanate:

2.73 lb. of available chlorine per pound of CN^- and

3.08 lb. of NaOH per pound of CN^-.

Oxidation of cyanide to $CO_2 + N_2$:

7.3 - 7.6 lb. available chlorine per pound of CN^- and

6.6 - 6.8 lb. of NaOH per pound of CN^-.

These are stoichiometric requirements; sometimes it is necessary to add excess reagent to accelerate the reaction.

If copper is present, it is necessary to add .51 pound of available chlorine per pound of copper. Also, if nickel is present, the addition of 2.2 pounds of chlorine per pound of nickel is required. Both of these metals will increase the detention time necessary for complete destruction of cyanides. The concentrations of treatable cyanides is very wide, from extremely high concentration (> 50,000 ppm) to low concentrations (< 5 ppm). The chlorine reaction is exothermic, causing a definite rise in bath temperature. The temperature increases as a function of cyanide concentration.

c. Economic Survey

The choice of chlorine gas or hypochlorites depends on the particular design needs. Chlorine gas is less expensive than direct hypochlorite treatment, but equipment costs are higher.

1. <u>Concentrated Cyanide Treatment Operational Expense</u>

Operation: 4000 gal/month
24 hr/day
20 day/month

Influent: 70,000 mg/1 total CN$^-$

Item	Yearly Cost	
	Small Lot Purchase	Large Lot Purchase
Capital Cost	2,637[1]	2,637[1]
Chlorine	25,133 - 61,690[2]	15,994 - 20,563[2]
Caustic	95,962 - 118,810[3]	54,835 - 63,974[3]
Electricity	57.60 - 230.40[4]	54.60 - 230.40[4]
Operating Labor	3,600	3,600
Maintenance	875	875
	$128,264 - 187, 842	$77,990 - 91,879

(1) Capital Cost = $15,000

Annuity Factor of .1458 = $3,637/year

(2) $\dfrac{8 \text{ lb } Cl_2}{\text{lb CN}} \times 119 \dfrac{\text{lb CN}}{\text{day}} \times \dfrac{(\$.11 - .27/\text{lb small lot})}{(\$.07 - .09/\text{lb large lot})}$

(3) $.21 - 26/lb small lot
$.21 - .14/lb large lot

(4) 1 KW/day @ $.01 - 04/KW

(All figures based on 1975 prices.)

2. Dilute Cyanide Treatment Operational Expenses

Operation: 250,000 gpd
24 hr/day
300 day/yr

Influent: 3 mg/l total CN⁻

Item	Yearly Cost	
	Small Lot Purchase	Large Lot Purchase
Capital Cost	900 [1]	900 [1]
Chlorine	2,046 - 5,022 [2]	1,302 - 1,674 [2]
Caustic	6,250 - 7,728 [3]	3,571 - 4,166 [3]
Electricity	72 - 228 [4]	72 - 288 [4]
Operating Labor	2,250	2,250
Maintenance	625	625
	$12,143 - 16,823	$8,720 - 9,903

[1] Total Cost = $6,250

Annuity Factor of .1758

[2] $62 \frac{lb.}{day}$ Small Lot ($.11 - .27/lb small lot)
Large Lot ($.07 - .09/lb large lot)

[3] $6.2 \frac{lb\ Cl_2}{lb\ CN} \times \frac{8\ lb\ NaOH}{lb\ CN} \times$ ($.21 - 26/lb small lot)
($.12 - 14/lb large lot)

[4] 1KW @ .01 - .04/KW

(All figures based on 1975 prices.)

d. Operational Requirements

Alkaline chlorination, while having the capability of
destroying highly concentrated cyanide waste, is limited by
the excessive expense of the process. With conventional
commerical systems, the plant may be automated with emergency
warning systems monitoring pH and possible toxic materials
formation. Complete destruction requires an extra holding tank
to increase detention time and limit shock loading.

Batch systems would require a minimum of manpower, and training
would be limited to specific needs. Fluctuations of waste con-
centrations are less significant with this method.

e. Process Hazards

Alkaline chlorination requires continuous monitoring of
pH to prevent production of cyanogen chloride and nitrogen trichloride.
Chlorine gas leaks and handling are a possible health hazard.
Possible production of large amounts of toxic sludge may require
secondary treatment. Also, the heat of reaction from chlorine
and cyanide combination may require some form of temperature control
before effluent can be sent to sewer.

f. Process Effectiveness

The overall process is effective within particular design
parameters. Effluent concentrations are below maximum allowable
limitations and toxic materials in sludge are dependent on initial
solution type. Alkaline chlorination is very ineffective on
iron complexed cyanides and relatively slow on nickel bearing
cyanides. This method is most common but is extremely expensive
and newer processes being developed should be considered first.

(References cited: 4, 5, 10, 22, 24, 29, 45, 52, 55, 78, 84, 95, 96.)

2. Electrolytic Chlorination

   a. Process Description

        A process known as electrolytic chlorination has been developed to destroy cyanide wastes. An electrolytic cell is used to produce chlorine which can react with the cyanides. Salt (1-3% solution) is added to provide the chlorine ion. This is accomplished by:

$$2NaCl + 2H_2O \longrightarrow 2NaOH + Cl_2 + H_2$$
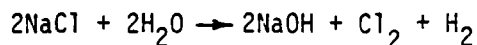
Caustic addition is not required since it is generated in the formation of chlorine. The chlorine-cyanide reactions are similar to alkaline chlorination. The chlorine is reduced to chloride ion during the oxidation of the cyanide, then the chloride ion is used again, in reaction with the anode, to reform chlorine. Treatment times are governed by equipment limitations which produce the chlorine; they run from 30 minutes to a few hours. The salt component is added by volumetric chemical feeder to maintain proper concentration. Formation of solids during treatment are removed by gravity sedimentation. The system process is manually operated. The electrolyte cells are protected by low flow and over voltage controllers. A temperature indicator, process timer, dc voltmeter and ammeter are needed. Oxidation is usually done by batch processing to insure complete treatment and prevent excess chlorine in the effluent. (See Figures #5 and #6.)

   b. Treatment Parameters

        The electrolytic system is capable of handling extremely varied concentrations of cyanides, from below 3 ppm to over 70,000 ppm. Operation is at room temperature and total flow with available systems is up to 250,000 gpd. The system size is

Process Flow Schematic
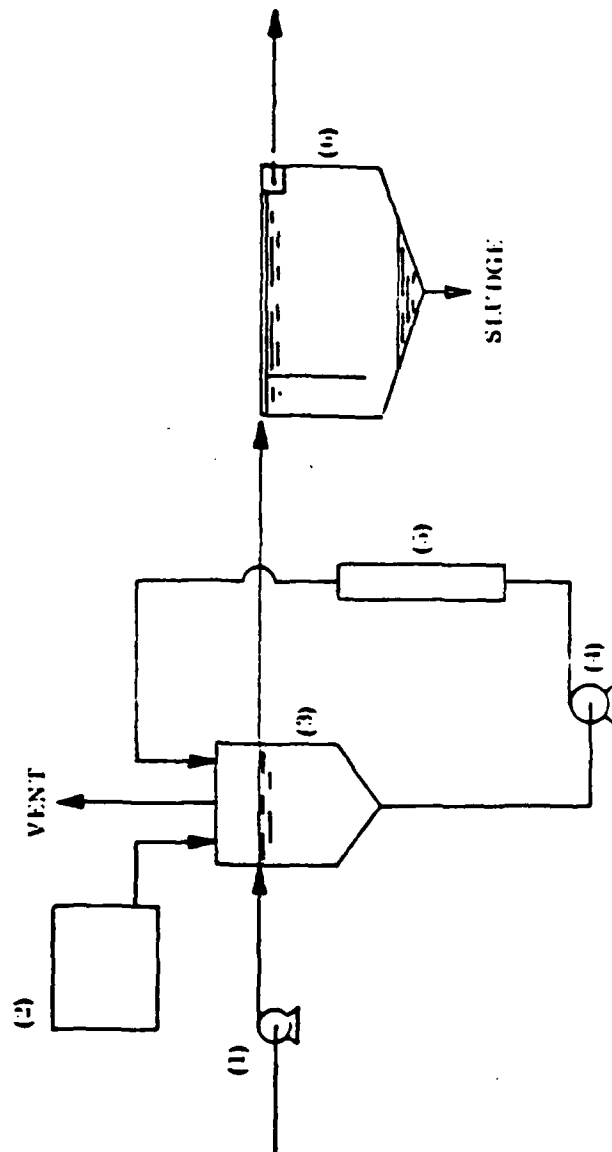
(Figure #5)

(1) PROCESS PUMP

(2) SALT FEEDER

(3) CHLORINATION TANK

(4) RECYCLE PUMP

(5) ELECTROLYTIC CELL

(6) SETTLING TANK
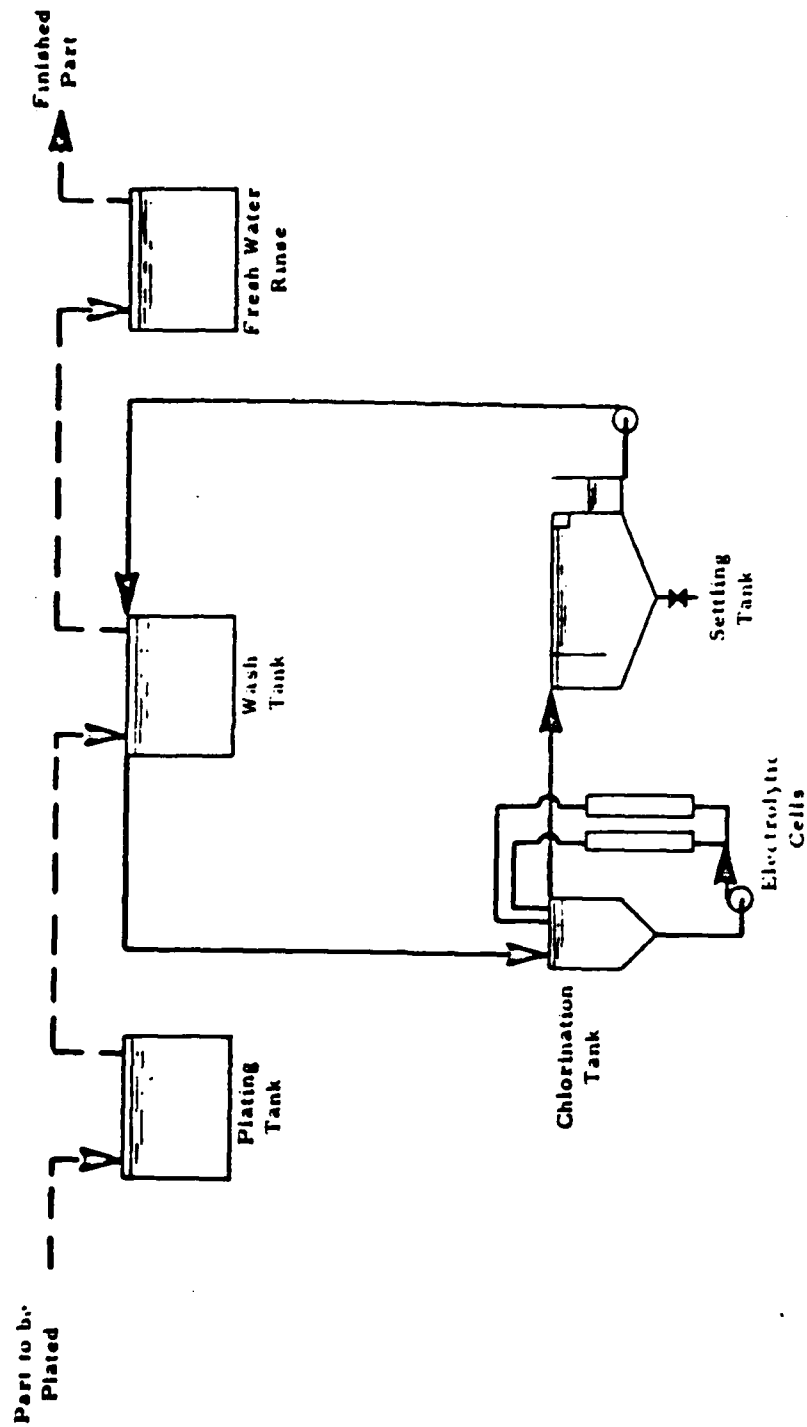
Integrated Cyanide Destruct Process With
Total Recycle Using Diluted Treatment System

(Figure #6)

limited to the maximum amount of chlorine producable, and banks
of electrolytic cells give unlimited potential. An adequate
water supply is necessary for concentrated systems.

d. Economic Survey

There are two commerically available electrolytic cells
considered for this system. They are the "PEPCON" and "CLOROPAC"
cells. The specific characteristics are:

	PEPCON	CLOROPAC
Life	2 years	5 years
Capacity 50% eff.	17 lb Cl_2/day	$\dfrac{14 \text{ lb } Cl_2}{\text{day}}$
90% eff.	31 lb Cl_2/day	$\dfrac{25 \text{ lb } Cl_2}{\text{day}}$
Power Required	500 amp @ 6 volt	200 amp @ 12 volt

Typical expenses based on two possible systems using PEPCON
cells are:

General estimates of 50¢/lb CN to $1.10/lb CN have
been given. These depend on cell type, salt concentration,
influent type and chlorine produced.

1. <u>Concentrated Cyanide Treatment Operational Expense</u>

Operation: 4000 gal/mon
24 hr/day
20 days/mon

Influent: 70,000 mg/l total CN$^-$

Item	Yearly Cost
Capital Cost	$11,824[1]
Electricity	11,550 - 44,880[2]
Anode Replacement	2,800
Catalyst	500
Maintenance	900[3]
Operating Labor	2,800[4]
Salt	660[5]
	$ 31,114 - 6,444

(1) 81,100 capital cost 10 years life (annuity factor .1458 assumed)

(2) 4,675 KW/day @ $.01 - .04/KW

(3) Maintenance material = $300

Labor $6/hr 100 hr/yr = $600

(4) 480 hr/yr @ $6/hr

(5) Salt 550 lb/day @ $.05/lb

2. Dilute Treatment Operational Expenses

Operation: 250,000 gpd
24 hr/day
300 day/yr

Item	Yearly Cost
Capital Cost	$3,034[1]
Electricty	288 - 1,152[2]
Anode Replacement	160
Caustic	150[3]
Maintenance	560[4]
Operating Labor	1,800[5]
Salt	900[6]
	$7,242 - 8,106

(1) Capital Cost = $20,800

Annuity Factor .1458 assumed

(2) 96 KW.day @ (.$01 - .04/KW)

(3) 50 lb/day @ $10,100 lb

(4) Maintenance material - $200
Labor 60 hr/yr @ $6/hr = $360

(5) 300 hr/yr @ $6/hr

(6) Salt 550 lb/day @ .05/lb

(Based on 1975 prices. PEPCON cell assumed 50% eff.)

e. Operational Requirements

Operation of the concentrated system required dilution of 200 gallons of waste with 2,000 gallons of water, to give total treatable volume of 2,200 gallons. Salt was stored in a brine tank in liquid form and injected into the system. No caustic was necessary since the system is held at proper pH values. The reaction between cyanide and chlorine is exothermic and a heat exchanger was necessary to remove 65 Btu/min produced. Magnesium chloride was used to prevent buildup of hard water deposits in electrolyte cells. This system required minimal maintenance and inspection. Start-up, adjustments and salt addition required 2 man hours per day.

The dilute system operated on a continuous feed of 175 gpm. Salt was added in solid form and no dilution was necessary. Also, the heat of reaction was low enough that no control was needed. No catalyst was added since it is ineffective at low cyanide levels. There was need for addition of caustic to maintain the pH of 8.5. Solids removal was not necessary and daily operation labor is about 1 manhour. No special training is required to operate this system. Electrode replacement is necessary every 2 to 2.5 years. Carbonate and bicarbonate ions present, in the electrolyte solution, reduced chlorine generating efficiency.

f. Process Hazards

This process generates a small amount of hydrogen gas, which is formed by electrolysis with water at the cathode of the electrolyte cell. This can be removed by venting into the chlorination tank. The entire system should have pH, cyanide and chlorine monitoring to prevent the incomplete destruction of cyanides present. Depending on the system, some storage of caustic may

be necessary. Safety precautions along with corrosive resistant materials are required for caustic handling. Excessive carbonate and bicarbonate ions will reduce efficiency possibly to the point of incomplete cyanide removal.

g. Process Effectiveness

This process is cost effective for stated design parameters. There is significant savings over alkaline chlorination, and varied influent levels can be treated. Exit concentrations of cyanides are below .1 mg/l and the major effluent metal is sodium. Long term testing on consistency of effluent data should be done before final decisions are reached.

(Reference cited: 4, 7, 10, 22, 25, 55, 97.)

3. Ozone Oxidation

   a. Process Description

Disposal of cyanide waste by ozone oxidation is a potent method of treatment. Simple cyanides and readily disassociated complexes (Zn, Cd, Ag, Cu, Ni) are oxidized to cyanates by the following reaction: (See Figure #7.)

$$CN^- + O_3 \longrightarrow CNO^- + O_2$$

Ozone cyanide mass ratios' range from $1.85 \frac{mgO_3}{mgCN}$ to $3.8 \frac{mgO_3}{mgCN}$. Cyanates can be further oxidized according to the following equation:

$$2OCN^- + H_2O + 3O_3 \longrightarrow 2HCO_3^- + N_2 + 3O_2$$
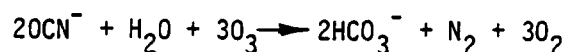
There are more stable cyanide complexes which are generally difficult to oxidize (iron). These have been treated with a combination of ultraviolet radiation and elevated temperatures. (See Figure # 8.) The ozone and cyanide reaction using ultraviolet radiation is:

$$XO_3 + NaCN + M(CN)_x \xrightarrow{UV} NaCNO + M(CNO)_x + O_2$$
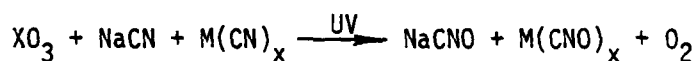
Ozone is produced when a high voltage arc is imposed across a discharge gap in the presence of a gas containing oxygen. The greater the concentration of oxygen the more efficient the ozone is produced. High temperatures build up in the discharge gap and unless efficient heat removal is accomplished the ozone decomposes rapidly.
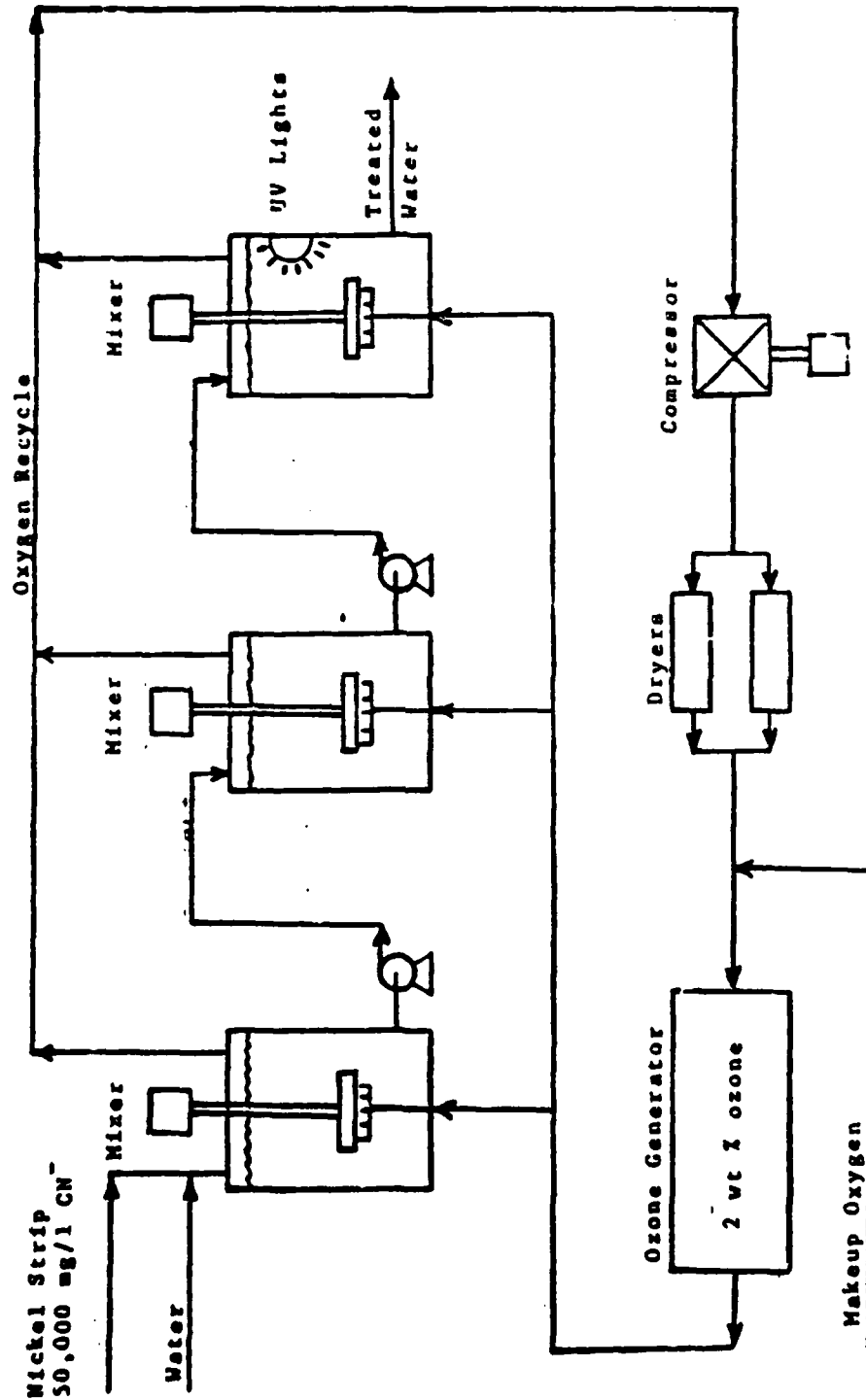
Full Size Cyanide Disposal System

(Figure # 7)

b. Treatment Parameters

The absorption and decomposition of ozone into water is tempera-
ture and pH dependant. More ozone can be abosrbed at lower tempera-
tures and decomposition is slower at pH values ($\leq$ 7). Reactions
can be optimized if a multi-stage unit is used. Reactions with
concentrated waste are limited by the rate at which ozone is trans-
ferred from gas to liquid phase, but in dilute waste, the rate of
oxidation is limited only by the chemical reaction rate. A
multi-stage unit is designed for optimum conversion of the cyanide
concentration to be treated in terms of pH, residence time,
temperature and UV light intensity. Decomposition of waste over
50,000 mg/1 is possible, but iron complexes should be below 4000
ppm. Flow rates are limited only by the maximum cyanide concentration
that the system can treat. Treatment times are directly related
to the amount and type of metal complex present. Cost analysis
for two possible ozone treatment systems without radiation are:

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1. <u>Concentrated Cyanide Treatment Operational Expense</u>

Operation: 3000 gpm
24 hr/day
20 day/month

Influent: 50,000 mg/1 CN⁻ total

Water Feed   2850 gph
3 gpm cooling water

Ozone Feed $2.4 \frac{\text{gm } O_3}{\text{gm CN-}}$

(150 lb CN/day)

Power Required   160,000 watts/day

Operation Cost $2.71/lb CN

Capital Investment $450,000 - 525,000

Capital Cost $4,000 - 4,500/lb CN

(based on one day CN treated)

2. <u>Dilute Treatment Operational Expense</u>

Operation: 49,000 gpd

Influent: 20 mg/1 CN total
$(1-1.5 \frac{\text{moles } O_3}{\text{mole CN}^-})$

Temperature   14-20 °C

pH: 7-9.5 Ozone Contactor
9-9.5 Final Clarifier

Catalyst   15% Caustic

Operation Cost $2.85/lb CN⁻

Total Cost $4.70/lb CN⁻

Capital Investment: $51,200

Note: Data for (1) and (2) based on 1975 prices.
(Water dilution cost not included.)

For CN $\leq$ 40 mg/1 $1.8 - 2.8 \frac{\text{mole}O_3}{\text{mole CN}}$

For CN $<$ 60 mg/1 $3 + \frac{\text{moles}O_3}{\text{mole CN}}$
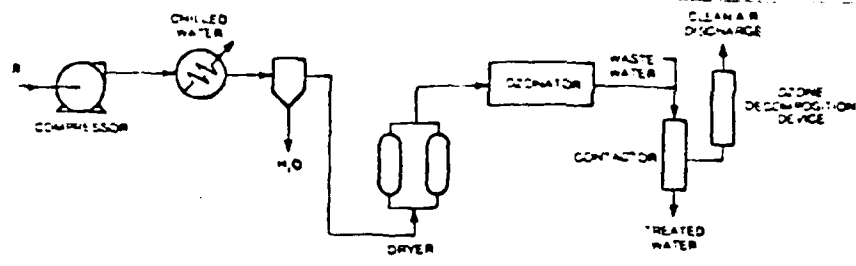
Once-through air process.
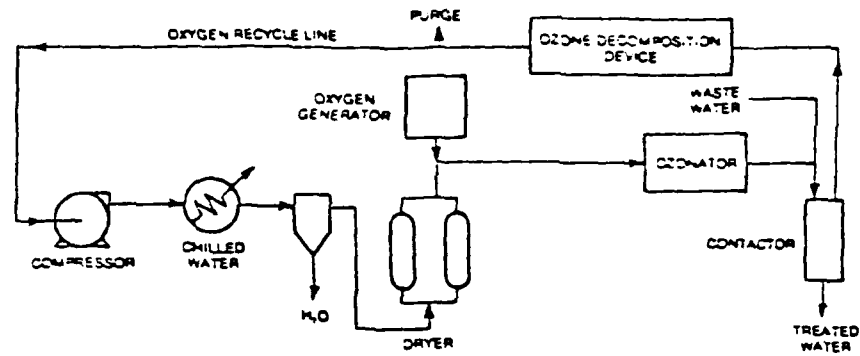
Oxygen recycle process.

(Figure # 8)

Cost Analysis for Ozone with UV Radiation

Operation: 1000 gal/week
24/hr day

Influent: 50,000 mg/1 CN total

Capital Investment	$217,000
Major Operating Costs	60 KW electricity/day = $216 - 864/yr (@ $.01 - .04/KW)
Maintenance	(8 manhours/wk @ $8/hr) = $3,328/yr UV light replacement = $5,000/yr
Total Yearly Operating Expense	$8,544 - 9,192/yr

(Based on 1975 prices.)

d. Operational Requirements

Most ozone treatment systems are automated and require little
special training. They can operate several weeks without shutdown.
If a UV system is incorporated, the annual replacement of lights
is necessary. Air cooled ozone generators have substantially
reduced maintenance and improved reliability over water cooled
systems.

e. Process Hazards

This sytem must have pH monitoring to prevent production
of hydrogen cyanide gas. There may be a need for caustic
depending on the system type. Corrosive resistant materials in
piping and storage may be required. If iron complexes are present
in appreciable amounts, a secondary test to insure complete destruction
of these cyanides are needed. The ozone generator produces
substantial heat which must be controlled to prevent excessive ozone
destruction. The relocation of compressors to outdoor protected
areas would help prevent overheating. The control of ozone in
solution is extremely important to the efficiency of cyanide
destruction. Excessive ozone concentration in the effluent may
pose potential pollution problems.

f. Process Effectiveness

Ozonation is a potentially excellent method of cyanide de-
struction. The initial investment costs are greater, but operation
costs are below that of other popular methods. If prices of
ozonation equipment are reduced, or as chemical prices rise, the
use of ozonation may become more attractive. The ability of this
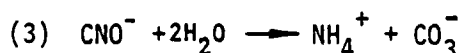system to destroy very concentrated cyanide solutions, and its

capability of breaking the stable iron complexes makes it a good
choice when these initial requirements are met.

(References cited: 10, 13, 19, 21, 26, 34, 35, 41, 48, 52, 61, 62,
79. 84, 90, 95.)

4. Electrolytic Decomposition

   a. Process Description

   Electrolytic destruction is one of the methods that has been used for cyanide destruction in industrial waste streams. The general procedure is to provide a treatment vessel such as a packed bed electrochemical cell. (See Figure #9.) Anodic current collectors and anodic beds are provided. The upper half of the cell contains cathodic current collectors and a packed cathodic bed. Electrolyte enters at the bottom of the cell and leaves from the top, thus each of the compartments contains a bed of electrically conductive and oppositely charged particles. The upper and lower beds are separated by a non-conductive membrane. When an aqueous solution of cyanides and heavy metals is passed through the cells, a direct current is applied. The metals are deposited upon the particles in the cathodic compartment and the cyanide is oxidized in the anodic bed. The resulting effluent contains low cyanide and metal concentrations. The cyanide oxidation is accomplished by this reaction:

   (1) $CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e$

   (2) $CNO^- + 2OH^- \longrightarrow CO_2 + 1/2\ N_2 + H_2O + 3e$

   (3) $CNO^- + 2H_2O \longrightarrow NH_4^+ + CO_3^-$
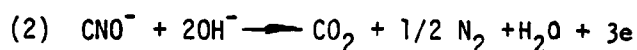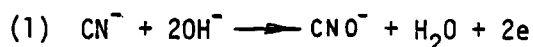
   *(Efficiency of this sytem increases when nickel is used as a catalyst.)

   b. Treatment Parameters

   Overall operational effectiveness is a function of temperature, pH, detention time and the current applied to the cell:
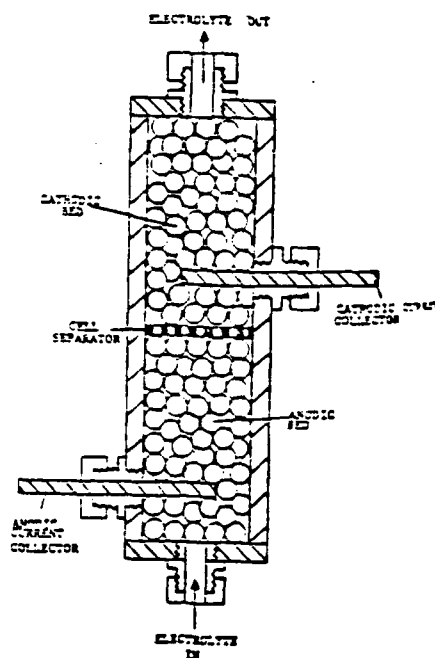
The packed-bed electrochemical cell.

⟨Figure #9⟩

T(°C)	Current (amps)	Running Time (hrs)	Initial CN^- (moles/l)	Final CN^- (moles/l)
81	0.5	140	2.5	.0025
	1.0	124	2.5	.006
	2.0	75	3.0	.0106
	4.0	54	2.0	.05
95	4.0	49	3.7	.025

For a dilute system, these were the operating requirements:

Solution Composition:	75 g/l CN^- total
Cyanide Destroyed:	1250 lb
Destruction Time:	18 days
Power Consumption:	3110 KWH
Water Consumption:	9000 gallons
Labor:	24 hrs total
Copper Salvaged:	400 lbs

c. Economic Survey

The overall operation of this system is simple and if costly metals can be recovered, the operating costs will be very low. This process requires little attention in operation. Initial concentrations are of little importance if they are high enough ($\geq$ 1000 ppm). There is little hazard of toxic compound formation, so control conditions are less important. The cell current used is directly proportional to the detention time, so the ability to judge needed power requirements is necessary. This system's effluent is not of low enough concentration for disposal and a secondary treatment is required, unless excessively long treatment times are used. The overall costs will depend on influent concentration, metals present, and the type of

secondary system needed. This process is most suited for large
electroplating bath treatment.

d. Operational Requirements

There are some control measures which will increase process
effectiveness and efficiency. Dilution water is provided mainly
to make up for evaporative losses in the cells, if temperatures
are kept low enough, this will be held at minimum. The electrodes
need to be separated enough to prevent shorting and if better quality
electrodes are used, maintenance time will be kept minimal. Cell
voltage should be kept between 2 to 40 volts, and a current of .1
to 5 amps must be provided to maintain oxidation. If a secondary
treatment system is used for the rinse tanks, the effluent from this
electrolytic system may be incorporated to decrease costs. Effluent
cyanide levels are less than 10 ppm and generally below 1 ppm.

e. Process Hazards

There is a slight possibility of hydrogen cyanide production
but normal supervision should prevent it. Process times must
be long enough to produce a sufficiently low cyanide concentration.
Buildup of cathodic deposits are possible along with potential shorting
of the system. If quality electrodes are used, with enough electrode
gas space, this can be controlled.

f. Process effectiveness

The electrolytic decomposition is practical and economical
when extremely concentrated cyanide solutions are to be
treated (> 1000 up to 100,000 ppm).

If secondary treatment systems are available to handle its low
effluent wastes, the use of this system is highly recommended.
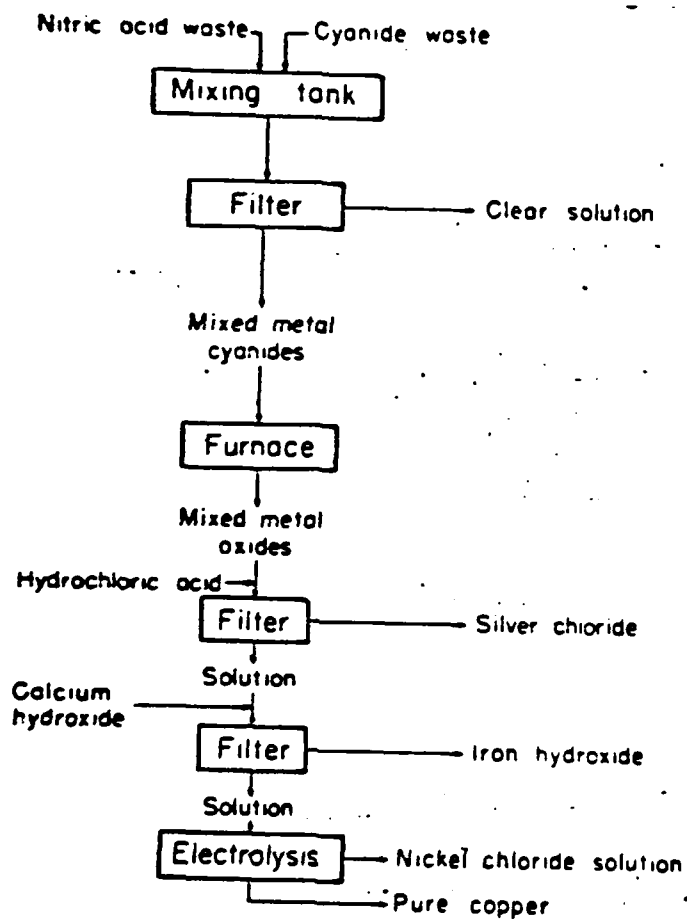If electricity and electrode costs are high, another method may prove

more cost efficient. However, if precious metal recovery can mean
substantial savings, the higher operating costs may be offset by
the recovery value.

(References cited: 8, 11, 20, 24, 30, 32, 48, 51, 55, 69, 72, 83,
 87, 88, 95.)

5. Waste Plus Waste

    a. Process Description

         The waste plus waste method is desinged to utilize one waste to treat a second waste and includes the recovery of most of the metal contained in both streams. One of the waste solutions must be alkaline containing cyanide and dissolved metals, while the other solution must contain acid and other dissolved metals. This process is especially applicable for the recovery of important dissolved metals such as nickel, chromium and silver. The process consists of slow addition of one waste containing acid to an alkaline liquid waste. The order of addition is critical to avoid the formation of hydrogen cyanide. The amount of dissolved metal in the two solutions must be equal or preferrably exceeding that amount required to precipitate all of the cyanide present. The reaction is carried out in a vessel equipped with stirring or agitation apparatus and an alkaline scrubber. (See Figure # 10.) Hydrogen gas, which may evolve during mixing and agitation, is scrubbed with a sodium hydroxide solution. In many cases helium gas is passed over the liquid surface and through a gas bubbler containing the .1 molar sodium hydroxide solution to collect the HCN gas. Batch processing is convenient, although it is possible to carry out the process continuously. During the reaction, the pH of the system is monitored and in no case should it fall below 4 to 4.5. When treating industrial wastes, a pH of 5.5 to 7.5 is kept to minimize the final effluent concentration of cyanide. The final product contains metal cyanides and a dilute solution of metal ions which is precipitated out and may be recovered.

Nitric acid waste — Cyanide waste

Mixing tank

Filter → Clear solution

Mixed metal cyanides

Furnace

Mixed metal oxides

Hydrochloric acid → Filter → Silver chloride

Solution

Calcium hydroxide → Filter → Iron hydroxide

Solution

Electrolysis → Nickel chloride solution
→ Pure copper

One variation of metal recovery process.

(Figure #10)

b. Treatment Parameters

For effective treatment, the pH of the system should be between 7.5 - 5.5. Adequate and controlled mixing is necessary for complete reaction to occur. Knowledge of metal types and con- centrations must be known for correct combination of wastes. The temperature will rise due to the exothermic reaction, so the initial solution temperature should be as low as possible. The flow rate is limited to the maximum safe mixing and reaction rate will minimize production of hydrogen cyanide gas.

c. Economic Survey

This system's economic incentive for treating electroplating wastes is the low cost of chemicals and the potential for recovery of valuable metals. The fact that waste acid can be used for neutralization reduces costs even more. Exact costs would depend entirely on the particular design, flow concentrations and availability of acid supplies. HCN gas control expenses must be included.

d. Operational Requirement

Operational requirements include pH and cyanide concentration control. The process should have adequate means of agitation and steady acid source flow. Operators would have to be able to control the input of all materials to an extent that no harmful gases are produced. Emergency systems warning of excessive cyanide gas production should be included.

e. Process Hazards

The potential production of large amounts of HCN gas, when the pH is altered, or mixing stopped, is possible. The sludge produced is toxic and disposal or refining is necessary. If control detention times are not met, the resulting cyanide effluent concentrations may be excessively high.

f. Process Effectiveness

This process works well on both dilute and concentrated wastes. It almost completely neutralizes the wastes to well below allowable levels. A large percentage of the expenditures involve corrosive piping costs and HCN gas control. Toxic sludges must be removed, however, costs may be reduced by metal recovery. This method is a very possible choice if a supply of waste acid is present with dissolved metals that can be used.

(References cited: 23, 48.)

III. <u>Processes Rejected for Cyanide Destruction</u>

1. Acidification

The large scale acidification of cyanide waste was rejected because of extensive pollution problems. This process involves introducing acid (sulfuric or hydrochloric) and removing hydrogen cyanide gas by aeration. The gas is then released to the atmosphere with large (60 - 100 ft.) stacks, or small stacks (25 - 50 ft.) with steam blown through to increase vapor dispersion. Sludge is precipitated and collects in the bottom of the tank where it can be dumped in landfills, or re-fined for valuable mineral contents. The effluent, after acidification, is released to the sewer. This process requires large amounts of acid, usually 14 pounds of acid per pound of cyanide. It must be completely sealed and resistant to all acid solutions. Acidification has been used effectively by large companies with high cyanide concentrations. It solves no problems except removing the wastes from the company's tanks.

2. Activated Carbon Absorption

The oxidation of cyanides by absorption on granular activated carbon was considered for specific plating needs. The treatment employs a copper catalyst, dissolved oxygen, and carbon. Carbon alone proved unfeasible but the addition of an effective oxidizing medium, in this case copper sulfate, improved results considerably. The presence of cupric ions results in the formation of copper cyanide complexes, which in the presence of oxygen, promotes cyanide oxidation and aids in the hydrolysis of cyanate. The development and feasibility of this process is limited by certain external variables. The process employs a packed, upflowing carbon bed thereby limiting the suspended solids concentration to less than 10 mg/l. Optimum efficiency was in the pH

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range of 7 - 8.5 and extraneous metals (especially iron) must be kept minimal. Specific oxygen concentrations and contact times must be maintained for acceptable accuracy. Concentrations of cyanides were limited to 50 mg/l and preferrably below 20 mg/l. Dilution of highly concentrated cyanide solutions with water was necessary.

This process, while producing low effluent cyanide levels, was decided to have too many restrictions on types of wastes and flow conditions to be acceptable. Costs were comparable to other systems, and if waste requirements could be met this would be an attractive alternative.

(Reference cited: 9, 10, 45, 46, 50, 70, 95.)

3. Biodestruction

Biological destruction of cyanide waste, in trickling filters and in activated sludge, by both aerobic and anerobic means, must be rejected for multiple reasons. The process is inhibited by the presence of metal ions such as those that would be found in electroplating wastes. Being a biological process, it is easily upset by such changes as temperature, pH and cyanide concentration. If destroyed, the biological population must be re-established requiring two to three weeks of growth plus re-acclimation to the cyanide concentration. Alternate treatment facilities must be available so as not to be faced with the choice of raw waste dumping or system shutdown.

Being a biological process, it cannot be as closely manipulated as other processes. A final disadvantage is that skilled technicians and constant supervision would be required to operate this treatment facility.

Increased labor costs and maintenance can be expected.

(References cited: 14, 47, 48, 53, 71.)

4. Dilution and Ponding

Dilution and ponding were both considered and immediately rejected. Dilution requires extremely large amounts of water and if this effluent were released in a stream or sewer it would cause extensive problems. The regulations on amounts of cyanide per million square feet of operation, effectively limits this practice.

Ponding allows cyanide concentrations to be decreased by releasing hydrogen cyanide gas to the atmosphere. It requires extensive space and precautionary measures to prevent hazards. This method converts a water pollutant to an air pollutant and does not solve the problems of cyanide treatment.

(References cited: 10, 25, 55, 76.)

5. Electrodialysis

Electrodialysis is a process where ions are transferred through anion or cation selective membranes by the driving force of an electric field. Transfer of ions is accomplished in a electrodialyizer stack which is an assembly of ion selective membranes, frame and membrane separators with electrodes and end plates.

The electrochemical processes in operation are primarily ion transport and, to some extent, electrolysis. This treatment was rejected due to its ability of only removing copper, zinc, cadmium, silver and gold. It is ineffective on other complexes such as iron and nickel. A second disadvantage is that it cannot reduce effluent levels to acceptable limits, therefore, secondary treatment would be required.

(References cited: 89, 91.)

6. High Pressure and Temperature Destruction

The complete destruction of solid and/or liquid cyanides by high pressure and temperature with the addition of a metal catalyst salt has been explored. Pressures of 5 - 100 atmospheres with temperatures between 140 - 180 °C were studied. Salts of iron, cobalt and nickel are used as catalysts, usually in amounts of 1 to 5 parts per 100 parts cyanide. This method produces ammonia and a salt of formic acid, with very low residual cyanide concentrations.

The energy costs, and construction of vessels to hold large enough amounts of waste influent would make this method cost prohibitive.

(References cited: 48. 73, 95.)

7. Hydrogen Peroxide

Hydrogen peroxide and a soluble metal compound added as a catalyst (including copper, silver, tungsten or vanadium) can be used to destroy cyanide wastes. This process has been emphasized for zinc plating firms with Dupont marketing the "KASTONE" system which is similar to the above.

There are several inherent disadvantages, including excessive decomposition of the hydrogen peroxide, unless mineral acid controls are used. Destruction of many cyanide complexes require special treatment.

Dupont's "KASTONE" process has been designed to handle different effluent types, but is is most suitable for small operations where complete system installation is favorable.

This process and Dupont's system were rejected due to the higher costs, limited use and inadequate research data provided.

(References cited: 10, 31, 48, 55, 59, 60, 95.)

8. Ion Flotation

Ion flotation was considered and rejected due to the incomplete data on collector effectiveness. The complex cyanide ion being negatively charged needs a anionic collector in order to effect flotation. Nickel, iron and cadmium complexes were ineffectively reduced with cyanide concentrations over 100 ppm; flotation could not be done on any of the collectors.

(References cited: 51, 95.)

9. Polymerization

Free cyanides have been removed from solution by polymerization, especially with amounts of formaldehyde. The resulting compound is a non-toxic polymer. At high temperatures and in the presence of ammonium salts, the process is faster and more effective.

The extensive problem of sludge formation and the untested effects on complexed cyanides resulted in this process being rejected for consideration. There were problems with effluent demands on the chemical and biological oxygen levels, which may lead to additional costs to degrade the polymer in a secondary treatment system.

(References cited: 18, 27, 66, 81, 95.)

10. Radiation

Radiation decomposition of waste cyanide solution is a simple and efficient method. It eliminates the detention time requirement caused by other methods, such as oxidation with chlorine. The process includes exposing cyanide ions, in solution, to penetrating ionizing radiation (preferably gamma radiation) until the cyanides have been decomposed into non-toxic constituents.

The reasons for rejecting this method were: the extremely high initial capital cost, operating cost, maintenance cost, need for highly skilled individuals to operate the system, danger to public health from high doses of radiation, and the probable difficulty in obtaining licensing for this type operation.

(References cited: 16, 57, 95.)

11. Selective Concentration Method for gold, silver and copper

Reverse osmosis is known to be useful in removing gold, silver and copper from plating wastes by employing cellulose acetate membranes. This process was rejected due to its applicability only on specific metals and its inability to remove cyanides in other complexes. The problem of scaling and membrane destruction, along with insufficient experimental data, confirms its unsuitability.

(References cited: 38, 39.)

12. Solvent Destruction

Cyanides have been removed from highly alkaline solutions by quaternary amines. This process is tailored to remove zinc and excess cyanide ions. An organic solvent diluent, such as diethylbenzene, is required to get the amine into solution. The stability of the many complex cyanides makes them most difficult to remove from the solvent and effective stripping was inadequate in most cases. This process is limited to specific metal types and concentrations; there has not been adequate re-searching to accept this method.

(Reference cited: 65.)

13. Starch Conversion Syrup

Cyanide compounds have been converted to biodegradable materials by treatment with a starch conversion syrup. Heavy metals are complexed with a chelating agent, preferably ethylenediaminetetraacetic acid or a salt thereof,to prevent them from interfering with the cyanide and sugar reaction. The resulting effluent is non-toxic and contains organics such as glucoheptonates. Reaction times vary from 15 minutes to 4 hours at temperatures between 100 °C and 18 °C respectively.

This method was rejected due to the inability of the conversion syrup to break down copper complexed cyanides and the susceptibility of the syrup and water mixture to bacterial and/or fungal growth. There was no specific operational data or cost analysis which confirmed the procedure effectiveness.

(References cited: 17, 95.)

TABLE 1

Comparison of Cyanide Concentration/Treatment Processes

Process	Advantages	Disadvantages	Cost	Rating
I. Concentration Techniques				
1. Ion Exchange	A. High effluent water quality B. Effective on free and complexed CN	A. High energy requirement B. Dilute CN concentrations only C. Sludge disposal difficult	Dependent on design and waste	
2. Evaporation	A. No discharge B. Cyanides and water recovered	A. High energy requirement B. Dilute CN concentrations only	Dependent on energy cost and design	3
II. Destruction Techniques				
1. Alkaline Chlorination	A. Widely used B. Inexpensive	A. Caustic storage B. HCN gas production C. Iron or Nickle CN slows reaction	Dependent of cyanide concentration and system design	1
2. Electrolytic Chlorination	A. Sodium Chloride used instead of chlorine gas B. Wide CN treatment range	A. Small HCN production B. Caustic storage may be necessary	$.50 to $1.10 per lb of CN	2

Process	Advantages	Disadvantages	Cost
3. Ozone Oxidation	A. Wide CN treatment range B. Low operational expense	A. High capital cost B. Stable complexes difficult to oxidize	$2.71 to $4.70 per lb of CN
4. Electrolytic Decomposition	A. Metals recovery possible	A. Economical only at high CN concentrations	Dependent on system design and metals recovered
5. Waste Plus waste	A. Wide CN treatment range B. Metals recovery possible	A. PH and temperature control critical B. Acidic waste needed	Dependant on availability of acid and design

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